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(54) Title: CATALYTIC PROCESS FOR MAKING HYDROFLUOROETHERS

(57) Abstract

Briefly, in one aspect, this invention provides a catalytic method of preparation of primary and secondary hydrofluoroethers, the process comprising reacting a fluorinated precursor material and an alkylating agent in the presence of a Lewis acid catalyst or a mixture comprising Lewis acid and Brønsted acid catalysts.

Catalytic Process for Making Hydrofluoroethers

FIELD OF THE INVENTION

This invention relates to a method of producing hydrofluoroethers. More

5 particularly, the present invention relates to the catalytic production of

hydrofluoroether compounds by the alkylation of certain carbonyl-containing

compounds.

BACKGROUND OF THE INVENTION

10 Chlorofluorocarbon compounds (CFCs) and hydrochlorofluorocarbon

compounds (HCFCs) as a class possess unique chemical stability and solvent

properties and have until only recently been used in a wide variety of applications,

finding utility in drying processes, cleaning processes (*e.g.*, the removal of flux

residues from printed circuit boards), and vapor degreasing applications. While

15 these materials were initially believed to be environmentally benign, they now are

linked to ozone depletion. According to the Montreal Protocol and its attendant

amendments, production and use of CFCs must be discontinued (*see, e.g.*, P.S.

Zurer, *Looming Ban on Production of CFCs, Halons Spurs Switch to Substitutes,*

CHEM. & ENG'G NEWS, Nov. 15, 1993, at 12). Characteristics sought in CFC and

20 HCFC replacements, in addition to low ozone depletion potential, typically include

low flammability, and low toxicity, and boiling point ranges that are suitable for a

variety of solvent cleaning applications. Such replacement solvents also should

have the ability to dissolve both hydrocarbon-based and fluorocarbon-based soils.

A group of compounds spotlighted recently as promising substitutes for

25 ozone-depleting solvents are hydrofluoroethers. These compounds, as a class, are

particularly promising candidates not only because of their zero ozone-depleting

potential, but also because they exhibit very useful solvent properties.

A number of synthetic routes to hydrofluoroethers are known. These

methods may be broadly divided into two groups; methods of fluorinating an ether

30 compound, and methods where the ether linkage is formed within a compound by

reaction with a fluorine-containing precursor. The former methods include: (1)

direct fluorination of an ether compound; and (2) electrochemical fluorination of an ether compound. The latter methods include: (3) the addition reaction of an alcohol to a fluorinated olefin; (4) alkylation of a partially fluorinated alcohol; and (5) non-catalytic alkylation of a fluorinated carbonyl compound with a suitable alkylating

5   agent. Japanese Patent No. JP 6-293686 provides a partial summary description of these varied methods.

      Suitable methods for alkylation of fluorinated compounds include those described by French Patent Publication No. 2,287,432 and German Patent Publication No. 1,294,949, and such useful non-catalytic alkylation processes

10   typically comprise the reaction of a perfluorinated acyl fluoride or a perfluorinated ketone with an anhydrous source of fluoride ion (*e.g.*, an alkali metal fluoride such as potassium fluoride, cesium fluoride, or silver fluoride) in an anhydrous polar, aprotic solvent to produce a perfluorinated alkoxide that subsequently is reacted with a suitable alkylating agent such as a dialkyl sulfate, an alkyl halide, or an alkyl

15   perfluoroalkanesulfonate, to produce a primary or secondary hydrofluoroether.

      A more recent advance with respect to the above alkylation processes is described by published patent application WO 96/36689 that provides a method of non-catalytic alkylation of fluorinated carbonyl compounds in the presence of a tertiary or aromatic amine.

20   While the alkylation processes described above may be commercially viable as they are practiced in the art, there is continuing need to improve the economic efficiencies of commercially employed methods of production. In the interests of optimizing the overall process, there also is an ever-present and strong interest in increasing product yields and purities and in decreasing raw material and waste

25   disposal costs. The elimination of potentially toxic alkylating agents such as the commonly used dimethyl sulfate from these reactions also would present significant safety benefits.

SUMMARY OF THE INVENTION

Briefly, in one aspect, this invention provides an improved alkylation process for the preparation of hydrofluoroether compounds, said process comprising:

5   (1) reacting in the presence of at least one Lewis acid catalyst or a mixture comprising Lewis acid and Brønsted acid catalysts:

a) a fluorinated ketene or a fluorinated carbonyl-containing compound of the formula:

$$R_f \left[\begin{array}{c} O \\ \parallel \\ C - X \end{array} \right]_n$$
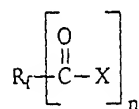
10   wherein n is an integer equal to 1, 2 or 3; and

when n is 1, R_f is a fluorine atom or is a fluorinated, preferably perfluorinated, alkyl group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic linear or branched and may optionally contain one or more

15   catenary heteroatoms such as nitrogen, sulfur, or oxygen;

when n is 2, R_f is a fluorinated, preferably perfluorinated, alkylene group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally contain one or more catenary heteroatoms

20   such as nitrogen, sulfur, or oxygen;

when n is 3, R_f is a fluorinated, preferably perfluorinated, alkylidene group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or

branched and may optionally contain one or more catenary heteroatoms

such as nitrogen, sulfur, or oxygen; and

wherein each non-fluorine substituent on the above R_f group may optionally

include -Cl, -H, -Br, -SO$_2$X, or –SO$_2$R' -COX, -CO$_2$R', or -OR' where R'

5   is a fluorinated or non-fluorinated alkyl group; and

wherein each X is independently a hydrogen or a halogen atom, preferably

fluorine, or is of the formula R'$_f$ or OR'$_f$ where R'$_f$ is a partially or fully

fluorinated or non-fluorinated alkyl group having from 1 to about 10

carbon atoms that may be substituted or unsubstituted, saturated or

10   unsaturated, cyclic or acyclic, linear or branched and may optionally

contain one or more catenary heteroatoms such as nitrogen, sulfur, or

oxygen; where X is an R'$_f$ group, that R'$_f$ group may form a ring with the

R_f group previously defined such as would give, e.g., a cyclic ketone;

and

15

b) an alkylating agent of the general formula:

R-F

wherein:

20   R is a substituted or unsubstituted, saturated or unsaturated, cyclic or

acyclic, linear or branched, non-halogenated or partially halogenated

alkyl group having from 1 to about 10 carbon atoms that can optionally

include one or more catenary heteroatoms such as oxygen, nitrogen or

sulfur, where if said R group is substituted, the non-hydrogen

25   substituents may optionally include -Cl, -Br, -F, -SO$_2$X', -SO$_2$R', -COX',

-COR', -CO$_2$R', or -OR' (where R' is as defined above and where X' is a

halogen atom, preferably F); and

(2) recovering hydrofluoroether product from the resulting mixture.

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In another embodiment, the present invention provides an alkylation process for the preparation of hydrofluoroether compounds, said process comprising:

(1) reacting in the presence of at least one Lewis acid catalyst or a mixture comprising Lewis acid and Brønsted acid catalysts:

5   a) a fluorinated mono- or polyether compound or a fluorinated oxacycloalkane with

b) an alkylating agent of the general formula:

R-F

10   wherein:

R is a substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched, non-halogenated or partially halogenated alkyl group having from 1 to about 10 carbon atoms that can optionally include one or more catenary heteroatoms such as oxygen, nitrogen or

15   sulfur, where if said R group is substituted, the non-hydrogen substituents may optionally include -Cl, -Br, -F, $-SO_2X'$, $-SO_2R'$ -COX', -COR', $-CO_2R'$, or -OR' (where R' is as defined above and where X' is a halogen atom, preferably F); and

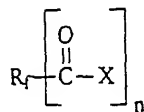20   (2) recovering hydrofluoroether product from the resulting mixture.

In yet another embodiment, the present invention provides an alkylation process for the preparation of hydrofluoroether compounds, said process comprising:

25   (1) reacting in the presence of at least one Lewis acid catalyst or a mixture comprising Lewis acid and Brønsted acid catalysts: .

a) a fluorinated mono- or polyether compound with

b) a fluorinated ketene or a fluorinated carbonyl-containing compound of

the formula:

$$R_f \left[\begin{matrix} O \\ \parallel \\ C-X \end{matrix} \right]_n$$

5   where R_f, X and n are as previously defined; and

(2) recovering hydrofluoroether product from the resulting mixture.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The catalytic processes provided herein afford myriad, important advantages

10   over other state of the art alkylation methods useful for the production of

hydrofluoroether materials. Among such advantages, the subject catalytic processes

may be carried out in the absence of additional solvent, a benefit that minimizes raw

material cost and improves reactor efficiency. Additionally, as compared to those

methods taught by the prior art, the methods of the invention do not require the use

15   of potassium fluoride, toxic alkylating agents such as dimethyl sulfate, phase

transfer agents, or amines such as trialkyl amines. These processes also produce no

waste salts and are not adversely affected by the presence of HF, a contaminant

commonly found in fluorinated starting materials. These reactions proceed rapidly

under mild conditions to achieve a relatively high yield of many hydrofluoroether

20   products while generating minimal undesired side products. The described methods

also can be adapted to continuous operation and, with the exception of spent

catalyst, generate negligible waste by-products.

The hydrofluoroether compounds made in accordance with the invention

may include those represented by the following general formula:

25   (I)

$$R_f\text{-}(O\text{-}R)_x$$

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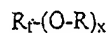
wherein x is 1 to 3; and

when x is 1, R_f is a fluorinated, preferably perfluorinated, alkyl group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or

5   branched and may optionally contain one or more catenary heteroatoms such as nitrogen, sulfur, or oxygen;

when x is 2, R_f is a fluorinated, preferably perfluorinated, alkylene group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or

10   branched and may optionally contain one or more catenary heteroatoms such as nitrogen, sulfur, or oxygen;

when x is 3, R_f is a fluorinated, preferably perfluorinated, alkylidene group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or

15   branched and may optionally contain one or more catenary heteroatoms such as nitrogen, sulfur, or oxygen; and

wherein each non-fluorine substituent on the above R_f group may optionally include $-Cl$, $-H$, $-Br$, $-SO_2X$, $-SO_2R'$ $-COX$, $-CO_2R'$, $-COR'$, or $-OR'$ where X a halogen atom, preferably F and where R' is a fluorinated or

20   non-fluorinated alkyl group; and

wherein each R is independently selected as a substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched, non-halogenated, or partially halogenated alkyl group having from 1 to about 10 carbon atoms where if R is substituted, the non-hydrogen

25   substituents may include $-Cl$, $-F$, $-Br$, $-SO_2R'$, $-SO_2X$, $-COX$, $-COR'$, $-CO_2R'$, or $-OR'$ where R' and X are as defined above, and where R may optionally otherwise also contain one or more catenary heteroatoms such as oxygen, sulfur or nitrogen.

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Examples of compounds suitable for alkylation according to the invention include fluorinated acyl halides, preferably fluorinated acyl fluorides, fluorinated aldehydes, fluorinated ketones and fluorinated ketenes; preferably such compounds are perfluorinated. Useful fluorinated ketenes include those of the formula:

5   (II)

$$R_f \backslash$$
$$\qquad C = C = O$$
$$R_f /$$

where each R_f is selected, independently from one another, as a fluorine atom or as a fluorinated, preferably perfluorinated, alkyl group having from 1 to about 15 carbon atoms that may be substituted or
10   unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally contain one or more catenary heteroatoms such as nitrogen, sulfur, or oxygen.
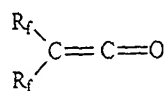
15   Other useful classes of carbonyl-containing compounds may be represented generally by the following formula:

                                                                                (III)

$$R_f \left[\begin{matrix} O \\ \| \\ C - X \end{matrix} \right]_n$$
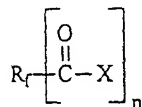
20
wherein n is an integer equal to 1, 2 or 3; and
            when n is 1, R_f is a fluorine atom or is a fluorinated, preferably perfluorinated, alkyl group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or
25   acyclic, linear or branched and may optionally contain one or more catenary heteroatoms such as nitrogen, sulfur, or oxygen;

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when n is 2, R_f is a fluorinated, preferably perfluorinated, alkylene group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally contain one or more catenary heteroatoms

5   such as nitrogen, sulfur, or oxygen;

when n is 3, R_f is a fluorinated, preferably perfluorinated, alkylidene group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally contain one or more catenary heteroatoms

10   such as nitrogen, sulfur, or oxygen; and

wherein each non-fluorine substituent on the above R_f group may optionally include -Cl, -H, -Br, -SO$_2$X, -SO$_2$R' -COX, -CO$_2$R', or -OR' where R' is a fluorinated or non-fluorinated alkyl group; and

each X is independently a hydrogen or a halogen atom, preferably fluorine,

15   or is of the formula R'$_f$ or OR'$_f$ where R'$_f$ is a partially or fully fluorinated or non-fluorinated alkyl group having from 1 to about 10 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally contain one or more catenary heteroatoms such as nitrogen, sulfur, or oxygen; where X is an

20   R'$_f$ group, that R'$_f$ group may form a ring with the R_f group previously defined such as would give, $e.g.$, a cyclic ketone.

Among the classes of carbonyl-group containing compounds depicted above by Formulas II and III useful as starting materials for the process invention are the

25   following, representative examples:

CF_3CF_2COF $CF_3CFHC(O)F$ $FCOF$

                                   CF_3COH $FCOH$

$$CF_3CF_2 - \overset{\overset{\displaystyle O}{\|}}{C} - CF\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{\diagdown}}$$

CF_3COF CF_3COCF_3 $CF_2{=}CFCOF$

$C_3F_7COCF(CF_3)_2$ $(CF_3)_2CFCOCF(CF_3)_2$ $(C_2F_5)_2NCF_2CF_2COF$

 $O\diagup\!\diagdown F\ N{-}C_2F_4COF$ $O\diagup\!\diagdown F\ N{-}CF_2COF$ $C_3F_7OCF(CF_3)C(O)F$

$CF_3COCF{=}CFCF_3$ $F{=}O$ $F{=}O$

$(CF_3)_2C{=}C{=}O$ $F(O)CC_3F_6C(O)F$ $FC(O)CF_2CF_2OCF_2CF_3$

$C_3F_7C(O)F$ $(CF_3)_2CFC(O)F$ $((CF_3)_2CFCOCF_2)_2$

           $FSO_2C_3F_6C(O)F$
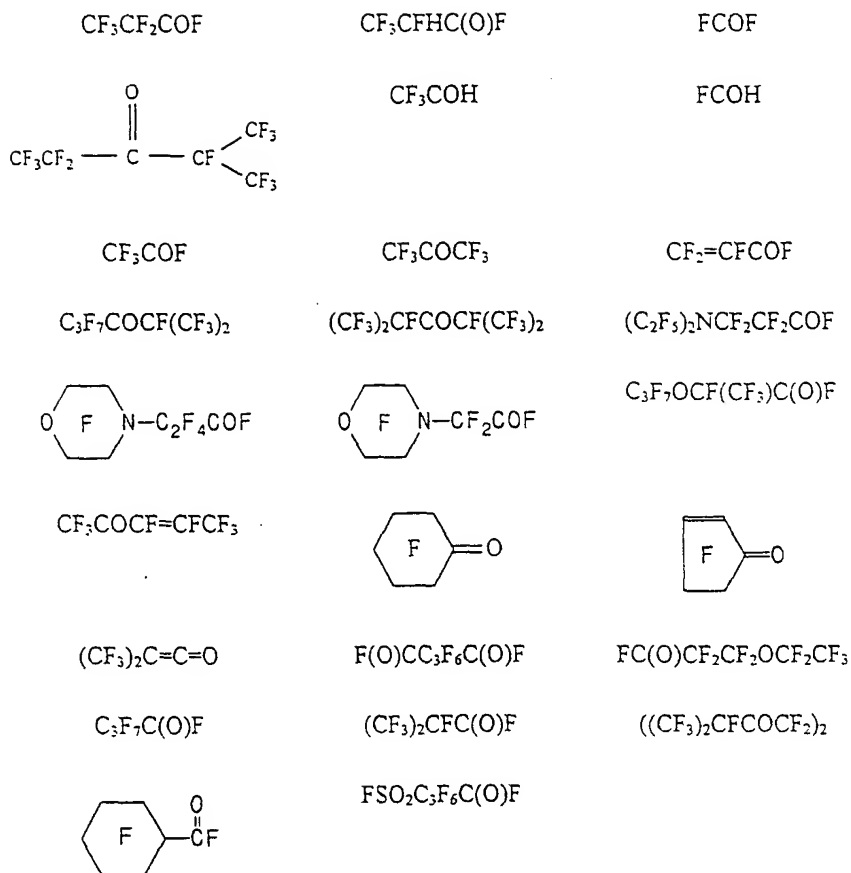
Useful perfluorinated acyl halides can be prepared, for example, by
electrochemical fluorination (ECF) of a corresponding hydrocarbon carboxylic acid,
5   or derivative thereof such as a carboxylic acid halide, anhydride or ester, using
either anhydrous hydrogen fluoride ("Simons" ECF) or KF.2HF ("Phillips" ECF) as
an electrolyte. Details of the "Simons" ECF process may be found in U.S. Pat. No.
2,519,983 (Simons) and by S. Nagase in 1 FLUORINE CHEM. REV. 77, 77-106
(1967). W.V. Childs et al, *Anodic Fluorination, in* ORGANIC FLUOROCHEMISTRY
10   1103-04, 1113-17 (Henning Lund & Manuel M. Baizer eds., 1991) provide a
description of the "Phillips" ECF process.

        Perfluorinated acyl halides and perfluorinated ketones also can be prepared by disproportionation of perfluorinated carboxylic acid esters (that can be prepared from the corresponding hydrocarbon or partially-fluorinated carboxylic acid esters by direct fluorination with fluorine gas). Disproportionation can be achieved by

5   contacting the perfluorinated ester with a source of fluoride ion (see the method described in U.S. Pat. No. 5,466,877 (Moore), whose description is incorporated herein by reference) or by combining the ester with at least one initiating reagent selected from the group consisting of: gaseous, non-hydroxylic nucleophiles; liquid, non-hydroxylic nucleophiles; and mixtures of at least one non-hydroxylic

10   nucleophile (gaseous, liquid, or solid) and at least one solvent that is inert to acylating agents. Alternatively, disproportionation can be achieved by contacting certain perfluorinated esters with a catalytic amount of an acid catalyst. This acid-catalyzed disproportionation may be effected in a prior step to produce perfluorinated acyl fluorides or may be used to generate perfluorinated acyl

15   fluorides *in-situ*. Acid catalysts that are effective in catalyzing the disproportionation of the perfluorinated esters include those claimed in the present invention.

        In one embodiment of the invention, carbonyl-containing compounds are generated *in situ* under the conditions of the catalytic alkylation process and the *in*

20   *situ* generated carbonyl compound may, in turn, be catalytically alkylated to form the hydrofluoroether product. Thus certain fluorinated compounds may be employed in the catalytic alkylation reaction that do not have a carbonyl group *per se*, but have a moiety that is readily converted to a carbonyl group under the conditions of this process, such as upon exposure to a Lewis acid catalyst or a

25   mixture of Lewis acid/Brønsted acid catalysts. These latter compounds include, generally, fluorinated mono- or polyether compounds and fluorinated oxacycloalkanes. Many useful mono- and polyethers include those described in U.S. Patent No. 4,357,282, whose description is incorporated by reference herein. Useful oxacycloalkanes can be substituted or unsubstituted, saturated and

30   unsaturated, and can be partially or fully fluorinated and include, for example, oxacyclopropanes, oxacyclobutanes and oxacyclopentanes. Oxacycloalkanes

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containing strained ring systems are most susceptible to acid-catalyzed
rearrangement to the ring opened carbonyl compound; thus oxacyclopropanes and
oxacyclobutanes are preferred.

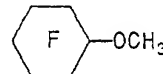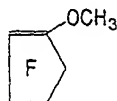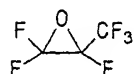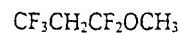Useful mono- and polyethers include those depicted by the formula:

5

(IV)
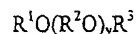
$$R^1O(R^2O)_yR^3$$

wherein y is 0 or is an integer greater than or equal to 1 and R^1, R^2, and R^3
10   each is independently selected as a non-fluorinated or a partially or fully
fluorinated, substituted or unsubstituted, linear or branched, cyclic or
acyclic, saturated or unsaturated alkyl group having from 1 to about 10
carbon atoms with the proviso that at least one of said R^1, R^2, or R^3
groups is fluorinated.

15

It must be understood with respect to the above fluorinated mono- and
polyether compounds, that while this class as described include compounds that are
potential products of the alkylation reactions of the invention, it may be desirable to
utilize the methods of this invention to convert one fluorinated ether into another,
20   and such conversions expressly are included within the scope hereof.
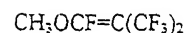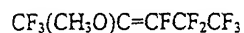
Representative of the above classes of compounds that do not contain a
carbonyl-group include, but are not limited to, the following:

$CF_3CFHCF_2OCH_3$ $(CF_3)_2CHCF_2OCH_3$ $C_4F_9OCH_2F$

$C_4F_9O(C_2F_4O)_2CF_2H$ $CF_3(CH_3O)C=CFCF_2CF_3$ $CH_3OCF=C(CF_3)_2$

$HCF_2CF_2OCH_3$ $C_6F_{13}OCHF_2$ $CF_3CH_2CF_2OCH_3$
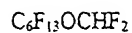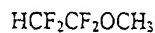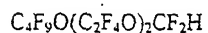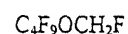
5   These compounds shown above may be used to generate useful carbonyl compounds in a prior step or *in situ*, as shown in the table below depicting the *in situ* conversion for representative starting ether compounds.

Starting Ether	*Generated Carbonyl Compound*	*Byproduct*
$CF_3CFHCF_2OCH_3$	$CF_3CFHCOF$	CH_3F
$(CF_3)_2CHCF_2OCH_3$	$(CF_3)_2CHCOF$	CH_3F
$C_4F_9OCH_2F$	C_3F_7COF	CH_2F_2
$HCF_2CF_2OCH_3$	HCF_2COF	CH_3F
$C_6F_{13}OCF_2H$	$C_5F_{11}COF$	CF_3H
	$CF_3(CO)C_2F_5 + C_3F_7COF$	-----
	$CF_3(CO)CF_3$	-----
$CF_3C(OCH_3)=CFCF_2CF_3$	$CF_3(CO)CF=CFCF_3$	CH_3F
$CF_3CH_2CF_2OCH_3$	CF_3CH_2COF	CH_3F

$(C_4F_9OC_2F_4O)_2CF_2$ $C_4F_9OCF_2COF$

$CH_3OCF=C(CF_3)_2$ $O=C=C(CF_3)_2$ + $F(CO)C(CF_3)=CF_2$ CH_3F

                                                                       CH_3F
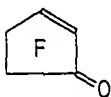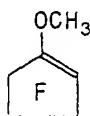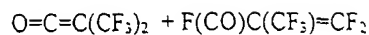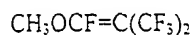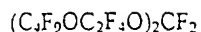
Fluorinated mono- and polyether compounds useful as precursors to carbonyl-containing compounds may be prepared by a variety of methods known in the art as previously described. Fluorinated oxacyclopropanes may be prepared, for example, by the oxidation of the corresponding fluorinated olefins using molecular oxygen, hypochlorite or other oxygen transfer agents. Fluorinated oxacyclobutanes and oxacyclopentanes may be prepared by the fluorination of the corresponding hydrocarbon oxacycloalkanes using a variety of fluorination techniques including direct fluorination, electrochemical fluorination or by the Phillip fluorination process. The latter materials also may be separated as by-products in the production of perfluoroacyl fluorides by electrochemical fluorination.

In another embodiment of the invention, carbonyl-containing compounds may be transformed *in situ* to isomeric or different carbonyl compounds under the conditions of the catalytic alkylation process, and the latter carbonyl compounds may, in turn, be catalytically alkylated. For example, a fluorinated ketene may undergo rearrangement to a fluorinated acid fluoride (or the reverse) which may then undergo catalytic alkylation to form a hydrofluoroether.

Alkylating agents useful for reaction with the carbonyl-group containing compounds or carbonyl precursors described above encompass any of a large number of known alkyl fluoride alkylating agents. It will be understood that the selection of a given alkylating agent will depend in large measure on the desired hydrofluoroether product; the alkyl group in the alkylating agent will determine one side of the ether linkage. Thus, for example, if 1-methoxy nonafluoroisobutane is a desired ether product, an alkylating agent having a methyl substituent (such as methyl fluoride) must be used. To ensure an adequate yield of desired product, the

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alkylating agent must be reacted with the fluorinated carbonyl-containing compound at least stoichiometrically, *i.e.*, in a 1:1 molar ratio. Preferably, however, to favor maximum yield, an excess of alkylating agent is used. Typically, the molar ratio of alkylating agent to carbonyl compound ranges from about 1:1 to about 5:1, and

5   preferably ranges from about 1.5:1 to about 2:1.

Useful alkylating agents include any of a large number of substituted and unsubstituted alkyl fluorides with one or more reactive C-F bonds. Any such substituents on the alkyl group may include $-Cl$, $-Br$, $-F$, $-COX'$, $-CO_2R'$, $-SO_2X'$, SO_2R', COR' or $-OR'$ (where X', R' and R are as hereinbefore defined), provided,

10   however, that the alkylating agent does not readily undergo competing side reactions under the catalytic alkylation conditions and that the alkylating agent does not deactivate the catalyst.

The most useful alkylating agents will be those described by the general formula:

15   (V)

$$R-F$$

wherein:

R is a substituted or unsubstituted, saturated or unsaturated, cyclic or

20   acyclic, linear or branched, non-halogenated or partially halogenated alkyl group having from 1 to about 10 carbon atoms that can optionally include one or more catenary heteroatoms such as oxygen, nitrogen or sulfur, where if said R group is substituted, the non-hydrogen substituents may optionally include $-Cl$, $-Br$, $-F$, $-SO_2X'$, $-SO_2R'$, $-COR'$,

25         $-COX'$, $-CO_2R'$, or $-OR'$ (where R' is as defined above and where X' is a halogen atom, preferably fluorine).

Representative alkylating agents include the following: CH_2F_2, CF_3H, CF_3CFH_2, CF_3CH_3, C_2H_5F, CH_3F, and $CFClH_2$. Preferred alkylating agents include CH_2F_2, CH_3F, and C_2H_5F.

It will also be understood that certain of the alkylating agents described

5   above by Formula V also may be generated *in situ*, for example: by the reaction of ethylene with hydrogen fluoride to produce ethyl fluoride; by the catalytic transhalogenation of an alkyl halide with a source of fluoride ion (*e.g.*, HF); or by the acid-catalyzed dealkylation of a hydrofluoroether as described in U.S. Patent No. 4,357,282 and incorporated herein by reference, such as is illustrated by:

10

(VI)

$$(CF_3)_2CHCF_2OCH_3 \rightarrow (CF_3)_2CHC(O)F + CH_3F$$
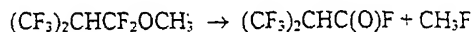
The alkylation process of the invention is accomplished by contacting the

15   fluorinated carbonyl compound and the alkylating agent with a small amount (normally not exceeding about 20 mol % of the limiting reactant) of catalyst or mixture of catalysts comprising one or more strong Lewis acids or a mixture of strong Lewis and strong Brønsted acids. Many of the catalysts and catalyst mixtures useful for this purpose are described by U.S. Pat. No. 4,357,282

20   (Anderson et al.) whose description is incorporated herein by reference. These acid catalysts may be liquids, solids or gases and may be supported on an inert substrate such as silica, graphite or alumina or on a polymeric support such as a fluorinated sulfonic acid resin (*e.g.*, Nafion™ resin available from DuPont); a technique particularly advantageous for continuous processing. In a preferred embodiment

25   liquid or gaseous reactants would react upon contact with a heterogeneous or supported catalyst in a stirred or fixed bed reactor.

Among the many useful acid catalysts are the following: SbF_5, $HSbF_6$, TiF_4, $AlCl_xF_{(3-x)}$ (x=0-3), HF-BF_3, TaF_5, NbF_5, AsF_5, BiF_5, ZrF_4, FeF_3, $SbCl_5$, $SbCl_2F_3$, $SbCl_xF_{(5-x)}$, $HOSO_2F/SbF_5$. Combinations and mixtures of these catalysts with each

30   other or with HF or FSO_3H also are considered useful.

Principally favored among these classes of catalysts is antimony pentafluoride, SbF₅, and catalyst mixtures containing SbF₅. Mixtures of HOSO₂F and SbF₅, including those sold under the commercial name "Magic Acid" and mixtures of SbF₅ and HF are particularly preferred. As is known, SbF₅ and HF
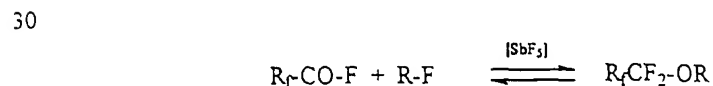
5   combine to form hexafluoroantimonic acid, HSbF₆, which is substantially less viscous than the normally highly viscous and polymeric antimony pentafluoride. Antimony pentafluoride may also be combined with other Brønsted acids, including CF₃SO₃H, H-N(SO₂CF₃)₂, and H-C(SO₂CF₃)₃. Antimony pentafluoride, as well as those mixtures containing it, also may be supported on a suitable inert solid

10   substrate. Such substrates include, but are not limited to, graphite, silica (fluorinated and not), titanium oxide (fluorinated and not), aluminum oxide (fluorinated and not), sulfonic acid resin, and any of a number of inorganic salts. Although catalysts may be used in the form of full- or partial fluorides, it is preferable for economic reasons to use as the starting catalyst non-fluorinated

15   materials such as chlorides. These may be converted to the corresponding fluorides or mixed halo-fluorides under the reaction conditions.

The desired reaction of the above reagents may be depicted generally by the equation:

20   $$\text{Fluorinated Carbonyl Compound} + \text{Alkylating Agent} \xrightleftharpoons{\text{[acid catalyst]}} \text{Hydrofluoroether}$$
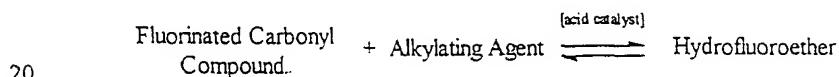
The reaction is a reversible equilibrium, the position of which is determined by the thermodynamic parameters ($\Delta G°$, $\Delta H°$, $\Delta S°$) for the reaction and the

25   reaction conditions. High conversions to hydrofluoroether products are favored by large negative values of $\Delta G°$. Where the alkylation reaction is exothermic (negative $\Delta H°$), conversions generally increase as the reaction temperature is lowered.

More specifically, in reference to Formula III above, where X is F and where n is 1, the reaction may be depicted as:

30   $$R_f\text{-CO-F} + \text{R-F} \xrightleftharpoons{\text{[SbF}_5\text{]}} R_f\text{CF}_2\text{-OR}$$

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and where X is R'$_f$ and n is 1:

$$R_f\text{-CO-R}'_f \ + \ R\text{-F} \quad \xrightarrow{[SbF_5]} \quad R_fR'_fCF\text{-OR}$$

5
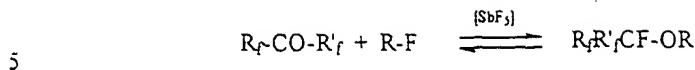
which for a typical specific reaction scenario of an acid fluoride can be represented as:

$$C_3F_7COF \ + \ CH_3F \quad \xrightarrow{[SbF_5]} \quad C_4F_9OCH_3$$

10
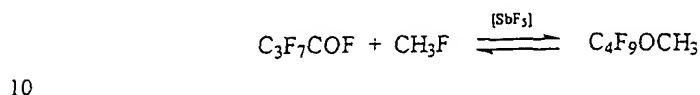
and for a typical reaction scenario for a ketone can be represented as:

$$C_3F_7COCF_3 \ + CH_3F \quad \xrightarrow{[SbF_5]} \quad C_3F_7(CF_3)CFOCH_3$$

15
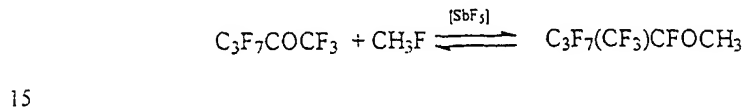
    The reaction of the perfluorobutyrylfluoride with CH$_3$F in the presence of antimony pentafluoride as described immediately above proceeds rapidly under mild conditions in the absence of solvent to produce the hydrofluoroether, which remains in equilibrium with the two starting materials. Because the reaction is a reversible

20   equilibrium, the amount of hydrofluoroether product produced is highly dependent on reaction conditions, and is particularly dependent upon temperature as well as upon the CH$_3$F concentration and pressure. This reaction, found to be exothermic (*i.e.*, having a negative standard enthalpy of reaction) in the forward direction, may be manipulated to maximize hydrofluoroether yield by cooling the reaction mixture

25   or by increasing the CH$_3$F concentration or pressure. Also in reference to the above reaction, the position of its equilibrium is isomer dependent; higher yields of hydrofluoroether may be obtained, for example, from the normal isomer of perfluorobutyrylfluoride than with its *iso* isomer under identical reaction conditions.

    In another embodiment of the invention, the reacting carbonyl moiety and

30   the alkylating agent may be covalently linked and the catalytic alkylation reaction may occur in an intramolecular fashion to form a cyclic hydrofluoroether as shown below for a specific reaction scenario:

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$$F\text{-}CH_2CF_2CF_2COF \quad \underset{[SbF_5]}{\rightleftharpoons}$$
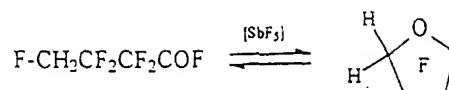
More generally, the alkylation methods of the invention may be performed in
any suitable reaction vessel that is compatible with the starting materials, products
and catalysts employed, although when volatile reagents are used, or when volatile
products are produced, a pressure vessel is preferred. The process may be carried
out by adding the fluorinated carbonyl-containing compound (or precursor), the
alkylating agent (or precursor), the acid catalyst, and if employed any solvent to the
reactor with moderate agitation at a temperature between approximately -120 °C
and 150 °C, preferably between about -70 °C and about 20 °C. These reagents may
be added to the reactor in any order. To minimize the possible occurrence of
undesired side reactions, however, the alkylating agent is preferably the last material
to be combined with the others.

The reaction equilibrium generally may be shifted to favor the
hydrofluoroether product by increasing the concentration (or pressure) of the
alkylating agent and/or by decreasing the reaction temperature. Where the
alkylating agent is a gas, the reaction should be carried out in a sealed pressure
vessel to prevent escape of the alkylating agent which if allowed to occur would
shift the equilibrium in the reverse direction and thereby compromise product yield.
Upon addition of all reagents to the reaction vessel, the mixture may be reacted at a
temperature between about -120 °C and about 150°C, preferably between -70 °C
and 20°C, and held at the reaction temperature until conversion to desired products
is essentially complete or until the desired equilibrium has been reached.

Once a desired equilibrium distribution is established, the reaction may be
quenched with a catalyst poison which essentially will terminate the equilibrium
reaction by deactivating the catalyst and allow isolation of the desired product(s).
Useful catalyst poisons for SbF_5 and HF/SbF_5 include numerous bases such as
alcohols (*e.g.*, methanol or ethanol), and water, olefins, carboxylic acids and
sulfides whose selection is well known in the art. Where a heterogeneous,

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supported, or biphasic (*i.e.*, two non-miscible liquid phases) catalyst is employed, it may be possible to terminate the equilibrium simply by isolating the reaction components from contact with the catalyst. This latter method may prove valuable in continuous processing schemes where fluorinated carbonyl compound and

5   alkylating agent are fed continuously to a suitable reactor system containing a heterogeneous, supported, or biphasic catalyst and where product hydrofluoroether is collected and separated from the effluent product stream. In such a scheme, quenching of the catalyst becomes unnecessary, and any unreacted carbonyl compound and/or alkylating agent may be recycled back to the reactor.

10   Hydrofluoroether product may be recovered from the product mixture of either a batch or continuous reaction process using any suitable separation process. Where acid fluorides are employed and the catalytic reaction is quenched with water or alcohol, any unreacted acid fluoride is converted to its corresponding carboxylic acid or ester, respectively. These may readily be separated from the

15   hydrofluoroether product using conventional distillation or extraction techniques. It will be understood that in carrying out the alkylation process as described herein, mixtures of hydrofluoroethers according to the general Formula I may be produced, including multiple isomers of a particular hydrofluoroether.

           Since Lewis acids are employed as catalysts, it is important that all starting

20   materials be of high purity and that the reactors be clean and dry to avoid catalyst deactivation that may be caused by certain adventitious impurities (especially basic impurities). Where acid fluorides are used as starting materials, the acid fluoride may be purified of catalyst poisons, for example, by extracting the acid fluoride with excess sulfuric acid for a period of three to five hours at room temperature followed

25   by one-plate distillation of the acid fluoride from the H_2SO_4 phase. To maximize reactor volume efficiency and to minimize costs, it also is preferred to conduct the catalytic reaction in the absence of solvent. But if desired, solvents may be used, provided they are weakly coordinating, non-basic solvents that will not deactivate the catalyst. For this reason, perfluorinated solvents (*e.g.*, alkanes, amines, and

30   ethers), SO_2, CF_3SO_3H, anhydrous HF, FSO_3H, SO_2ClF, and SO_2F_2 are preferred.

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The following examples are offered to aid in a better understanding of the present invention. This list is not to be construed as an exhaustive compilation of embodiments of the processes taught by this invention and the examples are not to be unnecessarily construed as limiting the scope thereof.

5

EXAMPLES

In the following examples, all acid fluorides were purified by fractional distillation prior to their use as reactants in the catalytic alkylation process. All

10 other reactants and reagents were used as purchased, without further purification unless otherwise specified. GC analyses were performed on a HP-5890 gas chromatograph equipped with a 1/8" OD stainless steel column packed with Supelco™ Carbopack C connected to a thermal conductivity detector or a 30 m X 0.32 mm ID glass capillary DB-5 column from J&W Scientific connected to a flame

15 ionization detector. GC-MS analyses were performed using an HP-5890 gas chromatograph equipped with a 105 m X 0.32 mm ID glass capillary RTX-200 column from Restek and interfaced with a Finnigan SSQ-70 mass spectrometer operating in chemical ionization or electron impact ionization modes. ^1H and ^{19}F NMR spectra were acquired using a Varian™ UNITY plus 400 FT-NMR

20 spectrometer operating at 400MHz and 376 MHz, respectively. NMR samples were spiked with a small amount of 1,4-bis(trifluoromethyl)benzene for use as a cross-integration standard in quantifying sample composition. Tetramethylsilane and $CFCl_3$ also were added as chemical shift zero references.

25 <u>Example 1</u>: Reaction of perfluorobutyrylfluoride (C_3F_7COF) with methyl fluoride (CH_3F) to produce perfluorobutylmethylether ($C_4F_9OCH_3$) using SbF_5 as a catalyst.

$$C_3F_7COF \ + \ CH_3F \ \overset{[SbF_5]}{\rightleftharpoons} \ C_4F_9OCH_3$$
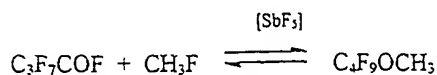
30 A 600 mL Parr™ Bench Top Mini Reactor (Series #4560) constructed of monel and equipped with a mechanical stirrer, thermocouple probe, dip tube, and pressure gauge was dried in an oven at 100 °C, transferred to a nitrogen filled

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drybox and loaded with 1.88 g of SbF$_5$ catalyst (Aldrich). The reactor was
reassembled and sealed under nitrogen in the drybox and then transferred to a
ventilation hood where it was chilled in a dry ice bath and evacuated to 10 mTorr.
The evacuated reactor was charged with 136.6 g of gaseous C$_3$F$_7$COF (Purity =

5   80.4 %, 69:31 *iso*:normal isomer ratio; major impurities include 15.5 % cyclo-
CF$_2$CF$_2$CF$_2$CF$_2$O, 1.3 % possible cyclo-CF$_2$CF$_2$CFClCF$_2$O and 1.3 % probable
CF$_3$CF$_2$CF$_2$OCF$_3$) while maintaining dry ice cooling. The reactor then was charged
in similar fashion with 29.8 g of gaseous CH$_3$F (Purity = 98⁻ %, available from
PCR).

10   Once all the reagents were charged, the dry ice bath was removed and the
reactor was allowed to warm gradually to 30 °C over a 1.5 hour period with
stirring. Heating was provided by a heating mantle and electronic temperature
controller. After this brief period of warming, the dry ice bath was replaced and the
reaction mixture was rapidly cooled to -25 °C and held at this temperature for

15   approximately 30 minutes with continued stirring. A ~5 mL sample (aliquot #1)
then was collected from the reactor by opening the valve on the dip tube and
allowing the positive pressure within the reactor to force out the cold, liquid
reaction mixture. The sample was collected under nitrogen in a dry-ice chilled
Schlenck™ tube containing approximately 30 mL of methanol to immediately

20   quench the antimony catalyst and convert any unreacted acid fluoride to the
corresponding methyl ester, C$_3$F$_7$CO$_2$CH$_3$. The remaining reaction mixture in the
reactor was allowed to cool further to -30 °C over a period of less than one hour
and was then quenched by charging 230 g of anhydrous methanol (at room
temperature and under nitrogen pressure) to the reactor with stirring (aliquot #2).

25   The methanol solutions comprising aliquots 1 and 2 were allowed to warm to
approximately 0 °C and then combined with approximately equal volumes of water
causing the nongaseous fluorochemical components to phase split as a lower liquid
phase which was separated, weighed and analyzed by gas chromatography. The
total amount of fluorochemicals recovered from aliquots 1 and 2, the composition

30   of each aliquot as determined by GC and GC-MS analysis, and the calculated

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percent conversion of acid fluoride to methyl ether from the GC results (overall and

independently for each isomer) is summarized in Table 1.

Table 1

Aliquot #	Reaction Temperature (°C)	Recovered Fluorochemical Yield	Fluorochemical Composition (by GC Area %)	Percent Conversion [ether]/([ether]+[ester]) x 100	
1	-25	7.4 g	38 % i-C$_4$F$_9$OCH$_3$ 31 % n- C$_4$F$_9$OCH$_3$ 31 % i-C$_3$F$_7$CO$_2$CH$_3$ 0 % n-C$_3$F$_7$CO$_2$CH$_3$	Overall Iso Normal	= 69 % = 55 % = 100 %
2	-30	83.1 g	52 % i-C$_4$F$_9$OCH$_3$ 31 % n- C$_4$F$_9$OCH$_3$ 17 % i-C$_3$F$_7$CO$_2$CH$_3$ 0 % n-C$_3$F$_7$CO$_2$CH$_3$	Overall Iso Normal	= 83 % = 75 % = 100 %

5

Only trace amounts (<<1 %) of other fluorochemical products were

detected by GC or GC-MS analysis, indicating that the catalytic alkylation reaction

is clean and produces few nongaseous side products. The relatively higher

10   conversions seen for the normal isomer compared to the iso isomer suggests that

branching in the R$_f$ group has a detrimental impact on the alkylation kinetics and/or

equilibrium constant. The isomer ratio in the recovered product is identical to the

starting acid fluoride, indicating that preferential decomposition of one of the

isomers does not occur under these reaction conditions.

15

Example 2: Reaction of perfluorobutyrylfluoride (C$_3$F$_7$COF) with methyl fluoride

(CH$_3$F) to produce perfluorobutylmethylether (C$_4$F$_9$OCH$_3$) using SbF$_5$ and HSbF$_6$

as a catalyst.

20
$$C_3F_7COF \ + \ CH_3F \ \xrightleftharpoons{[SbF_5/HSbF_6]} \ C_4F_9OCH_3$$
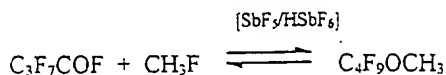
Using essentially the procedure of Example 1, the reactor was initially

charged with 1.03 g of SbF$_5$ catalyst (Aldrich). The reactor was reassembled and

25   sealed under nitrogen in the drybox and then transferred to a ventilation hood where

it was chilled in a dry ice bath and evacuated to 10 mTorr. The evacuated reactor

was charged with 68.3 g of gaseous C_3F_7COF (Purity = 80.7 %, 65:35 *iso*:normal

isomer ratio; major impurities include 12.2 % *cyclo*-$CF_2CF_2CF_2CF_2O$, 1.5 % *cyclo*-

$CF_2CF_2CF(CF_3)O$ and 1.1 % *cyclo*-$CF_2CF(CF_3)CF_2O$) while maintaining dry ice

5   cooling. The reactor was then charged in similar fashion with 22.1 g of gaseous

CH_3F (Purity = 98˙ %, PCR).

      Once all the reagents were charged, the dry ice bath was removed and the

reactor was allowed to warm gradually to 32 °C over a one hour period with

stirring and then rapidly cooled back to -22 °C. Gas chromatographic analysis of

10   reaction aliquots sampled at 10 °C and at -22 °C and quenched in methanol as

described in Example 1 indicated that significant alkylation of the acid fluoride to

produce *iso*- and *n*-$C_4F_9OCH_3$ had occurred. However the percent conversion

measured at -22 °C was not appreciably different from the conversion at 10 °C,

suggesting that catalyst poisoning had occurred. In order to restore catalytic

15   activity, an additional charge of catalyst comprising 1.0 mL of $HSbF_6$ (Aldrich,

triple-distilled) was added to the reactor at -80 °C via syringe. Once catalytic

activity was reestablished, the reaction mixture was allowed to equilibrate at various

temperatures for at least 5 minutes after which aliquots were removed and

quenched in methanol to permit determination by GC analysis of the equilibrium (or

20   near equilibrium) distribution of products and reactants. The procedure employed

to collect, quench, work up and analyze each reaction aliquot was similar to that

described in Example 1. The results of this study, including the composition of the

isolated fluorochemical phase and the calculated percent conversion at each

temperature are summarized in Table 2 below.

25

Table 2

Overall Reaction Time (min)	Reaction Temp. (°C)	Aliquot # (or comment)	Fluorochemical Composition (by GC Area %)		Percent Conversion [ether]/([ether]+[ester]) x 100	
321	10	3	6.8 %	i-C$_4$F$_9$OCH$_3$	Overall	= 37.1 %
			30.3 %	n-C$_4$F$_9$OCH$_3$	Iso	= 10.6 %
			57.6 %	i-C$_3$F$_7$CO$_2$CH$_3$	Normal	= 85.4 %
			5.2 %	n-C$_3$F$_7$CO$_2$CH$_3$		
395	30	4	1.6 %	i-C$_4$F$_9$OCH$_3$	Overall	= 24.9 %
			23.3 %	n-C$_4$F$_9$OCH$_3$	Iso	= 2.5 %
			62.1 %	i-C$_3$F$_7$CO$_2$CH$_3$	Normal	= 64.2 %
			13.0 %	n-C$_3$F$_7$CO$_2$CH$_3$		
1430	-4	5	16.4 %	i-C$_4$F$_9$OCH$_3$	Overall	= 45.1 %
			28.7 %	n-C$_4$F$_9$OCH$_3$	Iso	= 23.8 %
			52.6 %	i-C$_3$F$_7$CO$_2$CH$_3$	Normal	= 92.3 %
			2.4 %	n-C$_3$F$_7$CO$_2$CH$_3$		
1739	-19	6	35.2 %	i-C$_4$F$_9$OCH$_3$	Overall	= 64.6 %
			29.4 %	n-C$_4$F$_9$OCH$_3$	Iso	= 50.3 %
			34.8 %	i-C$_3$F$_7$CO$_2$CH$_3$	Normal	= 97.7 %
			0.7 %	n-C$_3$F$_7$CO$_2$CH$_3$		
1786	-22	Charged reactor with 4 psi (~200 torr) anhydrous HCl$_{(g)}$	----		----	
1862	-36	7	41.2 %	i-C$_4$F$_9$OCH$_3$	Overall	= 71.6 %
			30.4 %	n-C$_4$F$_9$OCH$_3$	Iso	= 59.2 %
			28.4 %	i-C$_3$F$_7$CO$_2$CH$_3$	Normal	= 100 %
			0 %	n-C$_3$F$_7$CO$_2$CH$_3$		
5861	22	8	13.8 %	i-C$_4$F$_9$OCH$_3$	Overall	= 27 %
			13.2 %	n-C$_4$F$_9$OCH$_3$	Iso	= 16.3 %
			71.0 %	i-C$_3$F$_7$CO$_2$CH$_3$	Normal	= 86 %
			2.1 %	n-C$_3$F$_7$CO$_2$CH$_3$		

    The dependence of the reaction composition on temperature, as reflected in
the measured distribution of quenching products and calculated conversions,
5   indicates that the catalytic alkylation reaction is a reversible equilibrium. The shift in
the reaction equilibrium in favor of the fluorinated ether products as the
temperature is lowered clearly demonstrates that the alkylation reaction is
exothermic; that is, the enthalpy of reaction, $\Delta H°$, is negative (in the forward
direction, as written). The persistence of catalytic activity following the addition of
10   a small amount of anhydrous HCl suggests that the catalyst is not readily
deactivated by trace chloride levels.

Example 3: Reaction of *iso-* and *n*-C_3F_7COF with difluoromethane (CH_2F_2) to form $C_4F_9OCH_2F$ using $HSbF_6$

$$[HSbF_6]$$
$$C_3F_7COF + CH_2F_2 \rightleftharpoons C_4F_9OCH_2F$$

5
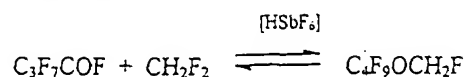
Using essentially the procedure of Example 1, the reactor was initially charged with 2.04 g of $HSbF_6$ catalyst (triple-distilled, Aldrich), then with 100.8 g of gaseous C_3F_7COF (Purity = 80.4 %, 69:31 *iso*:normal isomer ratio; major impurities include 15.5 % cyclo-$CF_2CF_2CF_2CF_2O$, 1.3 % possible cyclo-

10    $CF_2CF_2CFClCF_2O$ and 1.3 % probable $CF_3CF_2CF_2OCF_3$) while maintaining dry ice cooling. The reactor was then charged in similar fashion with 39.4 g of gaseous CH_2F_2 (Purity > 98%, PCR).

Once all the reagents were charged, the mixture was stirred rapidly and the reaction temperature was varied between 24 °C and -76 °C while collecting reaction

15   aliquots within this range to determine the effect of temperature on the distribution of reactants and products. Aliquots were removed through the dip tube and quenched under a nitrogen atmosphere in 100 % ethanol at dry ice temperature to destroy the catalyst and convert unreacted acid fluoride to the corresponding ethyl ester, as described in Example 1. The alcohol solutions were allowed to warm to

20   approximately 0 °C and then combined with approximately equal volumes of water causing the nongaseous fluorochemical components to phase split as a lower liquid phase which was separated, weighed and analyzed. The composition of each aliquot was determined by GC analysis, and GC peak assignments were verified by GC-MS and NMR analysis of selected samples. This data along with the calculated

25   percent conversions of acid fluoride to fluoromethyl ether (overall and independently for each isomer) is summarized in Table 3.

Table 3

Overall Reaction Time (min)	Reaction Temp. (°C)	Aliquot #	Fluorochemical Composition (by GC Area %)	Percent Conversion [ether]/([ether]+[ester]) x 100		
325	-55	4	1.1 % n-$C_4F_9OCH_2F$ 0.2 % sec-$C_4F_9OCH_2F$ 0 % i-$C_4F_9OCH_2F$ 34.7 % n-$C_3F_7CO_2CH_2CH_3$ 63.9 % i-$C_3F_7CO_2CH_2CH_3$	Overall	= 1.3 %
				Iso	= 0 %
				Normal	= 3.1 %
1328	-30	5	0.3 % n-$C_4F_9OCH_2F$ 0.3 % sec-$C_4F_9OCH_2F$ 0 % i-$C_4F_9OCH_2F$ 38.4 % n-$C_3F_7CO_2CH_2CH_3$ 60.9 % i-$C_3F_7CO_2CH_2CH_3$	Overall	= 0.6 %
				Iso	= 0 %
				Normal	= 0.8 %
1522	-75	6	3.2 % n-$C_4F_9OCH_2F$ 0.5 % sec-$C_4F_9OCH_2F$ 0 % i-$C_4F_9OCH_2F$ 37.6 % n-$C_3F_7CO_2CH_2CH_3$ 58.8 % i-$C_3F_7CO_2CH_2CH_3$	Overall	= 3.7 %
				Iso	= 0 %
				Normal	= 7.8 %
1701	-74	7	4.0 % n-$C_4F_9OCH_2F$ 0.4 % sec-$C_4F_9OCH_2F$ 0 % i-$C_4F_9OCH_2F$ 32.5 % n-$C_3F_7CO_2CH_2CH_3$ 63.0 % i-$C_3F_7CO_2CH_2CH_3$	Overall	= 4.4 %
				Iso	= 0 %
				Normal	= 11.0 %

    The data for the normal isomer illustrates the reversibility of this catalytic alkylation reaction and the sensitivity of the equilibrium position to temperature,

5   with the equilibrium shifting in favor of the ether product as the temperature is lowered. The lack of any measurable alkylation of the iso-C_3F_7COF isomer is further evidence of the detrimental impact of R_f branching on alkylation yields. The measurable but relatively low alkylation yields obtained for the normal isomer compared to similar reactions with CH_3F reflect the relatively less favorable

10   equilibrium constants for acid fluoride alkylations employing CH_2F_2 versus CH_3F as the alkylating agent. The source of the sec-$C_4F_9OCH_2F$ product isomer is not certain, although this product could be derived from alkylation of perfluoro-2-butanone ($CF_3CF_2COCF_3$) formed by $HSbF_6$ catalyzed rearrangement of the 4-membered ring cyclic ether, $cyclo$-$CF_2CF_2CF(CF_3)O$. The latter cyclic ether has

15   been detected as an impurity in ECF-derived perfluorobutyryl fluorides.

Example 4: Synthesis of perfluoroisopropyl methyl ether (i-C$_3$F$_7$OCH$_3$) from the HSbF$_6$ catalyzed reaction of hexafluoropropylene oxide (HFPO) with CH$_3$F by *in situ* formation of hexafluoroacetone as an intermediate.

(HFPO)

5
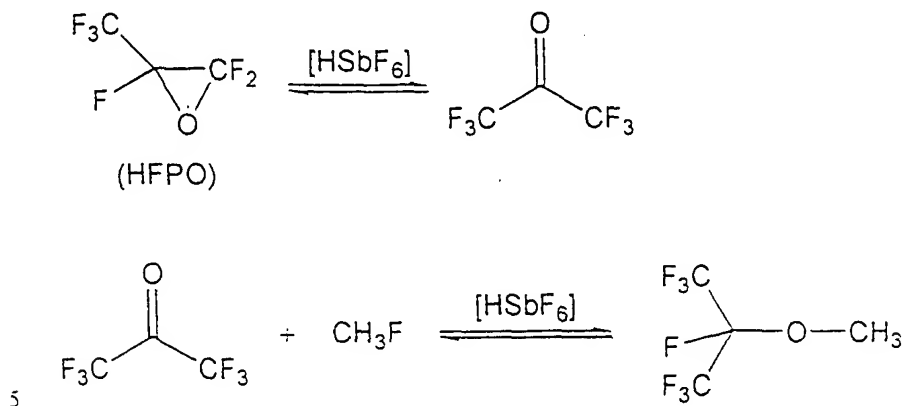
Using essentially the procedure of Example 1, the reactor was initially charged with 2.02g of SbF$_5$ catalyst (Aldrich) then with 66.7 g

10   hexafluoropropylene oxide (HFPO, Aldrich, 98 %) while stirring and maintaining dry ice cooling. A temperature increase to -28 °C was observed upon completion of HFPO addition. After stirring the reaction mixture for 10 minutes in a dry ice bath to allow the reaction temperature to return to -60 °C, the reactor was pressurized to 10 p.s.i. (775 torr) with nitrogen gas and a ~1 g sample of the cold reaction mixture

15   was removed through the dip tube and immediately quenched in 30 mL methanol at approximately -70 °C (aliquot #1), as described in Example 1. The resulting methanol solution was stirred for at least 30 minutes at -70 °C before gradual warming to room temperature to ensure complete methanolysis of the reaction components. The methanol solution then was analyzed by GC, GC-MS and NMR

20   in order to determine the distribution of quenching products.

It is known that HFPO reacts with methanol under these conditions to form CF$_3$CF(OCH$_3$)CO$_2$CH$_3$ whereas hexafluoroacetone gives primarily CF$_3$C(OH)(OCH$_3$)CF$_3$ along with small amounts of CF$_3$C(OH)$_2$CF$_3$ from hydrolysis. Therefore the relative amounts of these quenching products provides a

-28-

measure of the percent HFPO and hexafluoroacetone present in the reactor just
prior to quenching. As can be seen from the tabulated results for aliquot #1 in
Table 4 below, the reaction mixture at this point was comprised of approximately
98 % hexafluoroacetone, with only 2 % HFPO remaining unreacted.

5   The Parr reactor, with its remaining contents held at approximately -60 °C,
was then charged with 30.0 g of gaseous CH_3F (Purity = 98⁻ %, PCR) with stirring.
Methyl fluoride addition caused the reaction temperature to rise to -42 °C. The
reaction temperature was quickly returned to -70 °C through dry ice cooling and
this temperature was maintained for a period of hours during which additional

10   reaction aliquots were removed, quenched and analyzed (as described above) to
determine the reaction composition and percent conversion to the alkylation
product, i-$C_3F_7OCH_3$, as a function of time. The quenched reaction aliquots were
analyzed directly as the methanol solution. Additionally, in some cases, a portion of
the methanol solution collected was treated with an equal volume of water to cause

15   the liquid fluorochemical components to phase split as a separate lower phase which
was then isolated and independently analyzed by GC, GC-MS and NMR.
Alkylation was found to be essentially complete after 4.5 hours at -70 °C (following
the addition of methyl fluoride), as shown by the tabulated analytical data for
aliquot #3.

20

Table 4

Overall Reaction Time (min)	Reaction Temp. (°C)	Aliquot # (or comment)	Product Distribution in Methanol Solution by GC Area % (and Wt% by NMR)	Product Distribution in Fluorochemical Phase by GC Area % (and Wt% by NMR)
13	-60	1	CF₃C(OH)(OCH₃)CF₃ 97.2 % (98.1%) CF₃C(OH)₂CF₃ 0.5 % (0.7%) CF₃CF(OCH₃)CO₂CH₃ 2.3 % (1.2%)	—
17	-64	Begin charging CH₃F	—	—
285	-69	3	CF₃CF(OCH₃)CF₃ 98.3% CF₃CF(OCH₃)CF₂OC₃F₇ 1.6% CF₃C(OH)(OCH₃)CF₃ 0.02% CF₃C(OH)₂CF₃ 0% CF₃CF(OCH₃)CO₂CH₃ 0%	CF₃CF(OCH₃)CF₃ 92.4% (93.4%) CF₃CF(OCH₃)CF₂OC₃F₇ 7.1% (6.2%) CF₃C(OH)(OCH₃)CF₃ 0.1% (0%) CF₃C(OH)₂CF₃ 0% (0%) CF₃CF(OCH₃)CO₂CH₃ 0.3% (0.3%)

Thus, HFPO rapidly isomerizes almost completely to hexafluoroacetone in

5   the presence of catalytic amounts of $HSbF_6$ at low temperatures. The

hexafluoroacetone which is generated in situ in turn undergoes $HSbF_6$ catalyzed

alkylation by methyl fluoride at low temperatures and in nearly quantitative yield to

give the highly fluorinated ether, i-$C_3F_7OCH_3$. The only significant byproduct

detected is $CF_3CF(OCH_3)CF_2OC_3F_7$, which is believed to form by $HSbF_6$ catalyzed

10   dimerization of HFPO to the intermediate ketone, $CF_3COCF_2OC_3F_7$, which also is

then catalytically alkylated by methyl fluoride. Subsequent heating of the reaction

mixture to 0 °C after collecting aliquot #3 resulted in essentially no change in the

reactant/product distribution as determined by analysis of the methanol quenching

products. This indicates that either the alkylation equilibrium for hexafluoroacetone

15   is relatively insensitive to temperature, or that the $HSbF_6$ catalyst was somehow

inadvertently deactivated (or poisoned) prior to warming the reaction mixture.

Example 5: $HSbF_6$ catalyzed reaction of perfluoropropionyl fluoride (C_2F_5COF) with ethylene and excess HF to produce $n\text{-}C_3F_7OCH_2CH_3$ by *in situ* generation of ethyl fluoride (or its equivalent):

5

$$C_2F_5COF \; + \; CH_2{=}CH_2 \; + HF \; \underset{\longleftarrow}{\overset{[HSbF_6]}{\longrightarrow}} \; n\text{-}C_3F_7OCH_2CH_3$$
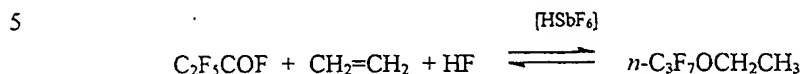
Using essentially the procedure of Example 1, the reactor was initially

10   charged with 1.798 g of $HSbF_6$ catalyst (Aldrich) and then with 71.80 g of gaseous C_2F_5COF (Purity = 97 %; Major impurities include 1.5 % $CF_3CF_2OCF_3$ and 0.5 % *cyclo*-$CF_2CF_2CF_2O$) while maintaining dry ice cooling. The reactor then was charged in similar fashion with 31.6 g anhydrous HF and 27.6 g ethylene (99.5[+] %, Aldrich), in that order. The ethylene was added slowly to minimize the reaction

15   exotherm.

        Once all the reagents were charged at -70 °C, the progress of the reaction was monitored as a function of temperature by periodically removing reaction aliquots through the dip tube and quenching in methanol as previously described in Example 1 to destroy the catalyst and convert any unreacted C_2F_5COF to the

20   corresponding methyl ester. The resulting methanol solutions were analyzed by GC after warming to room temperature. A portion of each methanol solution was treated with an equal volume of chilled water to cause the fluorinated components to phase split as a separate lower liquid phase. The liquid fluorochemical phase was isolated and analyzed independently by GC. Selected samples also were subjected

25   to GC-MS analysis to confirm GC peak assignments. Analytical results for each aliquot are summarized in Table 5 below. Since the methanol solution and the isolated fluorochemical phase for each aliquot gave virtually identical distributions of quenching products, only the results for the methanol solution are shown.

Table 5

Reaction Time (min)	Pressure (torr)	Temp (°C)	Aliquot # And Comments	Product Distribution in Methanol Solution by GC Area %
74	2740	-67	Addition of all reactants complete.	
146	2070	-70	Aliquot # 1	$C_2F_5CO_2CH_3$ 69 % n-$C_3F_7OC_2H_5$ 31 % [Alkylation Yield = 31 %]
300	1750	-70	Aliquot #2, Gradual pressure drop probably due to slow ethylene polymerization.	$C_2F_5CO_2CH_3$ 73 % n-$C_3F_7OC_2H_5$ 27 % [Alkylation Yield = 27 %]
362	2380	-16	Aliquot #3, Insoluble polyethylene oil observed as separate phase in MeOH quench.	$C_2F_5CO_2CH_3$ 64 % n-$C_3F_7OC_2H_5$ 36 % [Alkylation Yield = 36 %]
408	1030	-71	Aliquot #4, Insoluble polyethylene oil observed as separate phase in MeOH quench.	$C_2F_5CO_2CH_3$ 66 % n-$C_3F_7OC_2H_5$ 34 % [Alkylation Yield = 34 %]

The maximum conversion to n-$C_3F_7OC_2H_5$ measured was 36 %, similar to what was achieved in a separate experiment employing ethyl fluoride (instead of

5   ethylene + HF) as the alkylating agent (see Example 9). In addition to the quenching products listed in Table 5 above, later aliquots (#3 and 4) also contained significant quantities of a byproduct identified by GC-MS as a mixture of polyethylene oligomers, some of which contained a single fluorine atom. The polyethylene oligomers are presumably formed by acid initiated cationic

10   polymerization of the ethylene reactant, which apparently competes with the catalytic alkylation reaction, especially at elevated temperatures, and eventually appears to lead to catalyst poisoning. Similar evidence of ethylene polymerization was observed using ethyl fluoride as the alkylating agent (Example 9).

15   Example 6: This example describes experiments designed to assess the relative activities of various acids as catalysts for the reversible alkylation reaction shown below:

[Catalyst]

20   $$C_3F_7COF \ + \ CH_3F \ \rightleftharpoons \ C_4F_9OCH_3$$

-32-
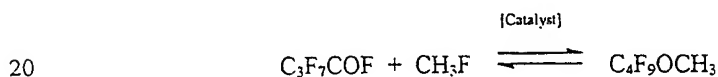
Since it has been established that this reaction is a reversible equilibrium, and

therefore governed by the principle of microscopic reversibility, any catalyst which

catalyzes the forward reaction will also catalyze the reverse reaction and vice versa.

Thus, a simple and convenient method was developed for catalyst screening which

5   involves the reaction of a pure sample of the hydrofluoroether, $C_4F_9OCH_3$ (65:35

iso:normal isomer mixture, available from 3M Company as HFE-7100™ fluorinated

fluid) with a small amount of each potential catalyst under ambient conditions and

qualitatively assessing catalyst activity by comparing the relative rates of

dealkylation. Barring interference from catalyst poisons, those catalysts which

10   provide the highest activity for dealkylation (reverse reaction) will be the most

active for alkylation (forward reaction) as well.

In the experimental procedure, a small amount, typically 0.1 to 0.5 grams, of

the potential catalyst was loaded into an oven-dried, 10 mL glass vial and

approximately 3 to 4 grams of the test hydrofluoroether was added at room

15   temperature with minimal exposure of the catalyst mixture to ambient air. The vials

were loosely capped to allow any evolved gases to escape. Catalyst activity was

judged qualitatively from the observed relative rates of gas ($CH_3F + C_3F_7COF$)

evolution and the extent of evaporative cooling of the reaction mixtures for each

catalyst. If no reaction was apparent at ambient temperatures, the contents of the

20   vial were heated briefly to reflux temperature using a hand held heat gun and the

vial monitored for apparent reaction. The formation of C_3F_7COF was confirmed by

its characteristic odor, and in some cases by quenching the partially converted

reaction mixture with methanol and identification of the methyl ester by GC

analysis. Since the screening reactions were conducted in ambient air and certain

25   catalysts are sensitive to poisoning by moisture and other agents, lack of apparent

activity in this screening test is not necessarily dispositive of catalytic activity. The

following results were obtained.

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a) SbF$_5$: The addition of the hydrofluoroether to antimony pentafluoride led to an instantaneous and rapid evolution of gas which was determined to be a mixture of C$_3$F$_7$COF and CH$_3$F. The reaction proceeds until the ether has been
5   completely consumed.

b) HSbF$_6$: In a similar manner, hexafluoroantimonic acid was found to be catalytically active at ambient temperature. As with SbF$_5$, the reaction occurs instantly and with rapid evolution of gas and continues until the hydrofluoroether has been completely consumed. The HSbF$_6$ appeared to be
10   slightly more active than SbF$_5$ under similar conditions.

c) 4 FSO$_3$H·SbF$_5$: This catalyst, available as Magic Acid™ from Aldrich Chemical Company, displayed catalytic activity comparable to HSbF$_6$. Reaction was instantaneous and gave rise to rapid gas evolution until all hydrofluoroether was consumed.

15   d) SbCl$_5$: Antimony pentachloride is soluble in the hydrofluoroether to give a clear slightly yellow solution. Although no gas evolution was noted at first, the solution gradually became cloudy with a white, milky appearance. On slight warming (body heat from hand), the solution became transparent once again and began to evolve gas. The gas was determined to contain C$_3$F$_7$COF by detection
20   of its very characteristic odor. Though not as immediately active as the previous two catalysts, antimony pentachloride does exhibit latent catalytic activity for this reaction.

e) AlCl$_3$: No catalytic activity was observed at ambient temperature, but upon heating to brief reflux C$_3$F$_7$COF was again detected by its odor. In this case, the
25   reaction did not proceed to completion.

f) AlCl$_n$F$_{(3-n)}$ (ACF) : This catalyst was prepared according to the method described in U.S. Pat. No. 5,157,171 , Example 1. The catalyst was stored and loaded into the glass test vial in a nitrogen-filled drybox in order to minimize exposure to moisture, which can reportedly lead to catalyst poisoning. Reaction

with the hydrofluoroether was conducted in ambient air as described above.
Initial catalytic activity was moderate, but significantly less than SbF$_5$. Also,
catalytic activity declined rapidly with time and was no longer detectable after 5
minutes, at which point most of the original hydrofluoroether charge still

5   remained. The rapid loss in catalytic activity in this instance may have been due
to poisoning by atmospheric moisture.

g) SiO$_2$/AlCl$_2$: This catalyst was prepared according to the method of R. Drago
in Inorg. Chem. 29, 1186 (1990) and handled in a fashion similar to that
described for ACF to minimize exposure to ambient moisture. Initial catalytic

10   activity was very low and, as with ACF, declined to the point where it was
undetectable in less than 5 minutes.

h) 1:1 HC(SO$_2$CF$_3$)$_3$/SbF$_5$ (by wt.) : The tris-(trifluoromethanesulfonyl)methane
acid was prepared according to the method described in U.S. Pat. No.
5,554,664, Example 1 and combined with an equal weight of SbF$_5$ in a nitrogen-

15   filled drybox. The catalyst mixture was loaded into a glass test vial and removed
from the drybox for subsequent reaction with the hydrofluoroether in ambient
air. Initial catalytic activity was moderate, comparable to ACF and significantly
less than pure SbF$_5$.

20   Example 7: In addition to determining the relative reactivities of various catalysts,
one can use test methods identical to those described above for Example 6 to
determine the relative reactivities of various hydrofluoroethers toward catalytic
dealkylation by a given catalyst at ambient temperature. When combined with
calculated thermodynamic parameters for a given equilibrium reaction, this

25   information can be useful in predicting whether a particular ether structure can be
more or less easily prepared by the catalyzed reaction of the appropriate carbonyl
precursor with an appropriate alkylating agent. One also gains insight into the
lifetime of the catalyst at room temperature in the presence of the various reaction
components by this test. The following results were obtained for a series of

30   different hydrofluoroethers using either SbF$_5$ or HSbF$_6$ as the catalyst where the

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indicated hydrofluoroether was reacted with the catalyst in the manner described in
Example 6.

a) $C_4F_9OC_2H_5$ (60:40, *n-* to *iso*): Catalytic dealkylation with $HSbF_6$ to produce
5   ethyl fluoride and C_3F_7COF is rapid initially, but the rate of reaction quickly
          decreases and then stops, possibly due to deactivation of the catalyst by the
          ethyl fluoride by-product. Further experiments demonstrated that $C_4F_9OC_2H_5$
          can be prepared from ethyl fluoride and C_3F_7COF at lower temperatures where
          the antimony catalysts retain their activity for significantly longer periods of
10   time.

b) *n-* and *i-*$C_4F_9OCH_3$: In a comparison of the rates of reaction of the normal and
          iso isomers, pure samples of each isomer were reacted with SbF_5 at room
          temperature. In these side by side experiments, the *iso* isomer was completely
15   consumed in 5 minutes whereas the normal isomer required 14 minutes.

c) $C_2F_5CF(OCH_3)CF(CF_3)_2$: $HSbF_6$ catalyst caused vigorous gas evolution at
          room temperature. The starting material was consumed completely and the
          product which remained in the flask was determined to be $C_2F_5COCF(CF_3)_2$ by
20   IR and GCMS analysis.

d) Methoxyperfluorocyclohexane: In this case, it was found that $HSbF_6$ did not
          rapidly catalyze the decomposition of the ether at room temperature. However
          SbF_5 did catalyze the rapid decomposition of the ether at room temperature to
25   give significant amounts of perfluorocyclohexanone, as determined by GC

e) $C_4F_9OCH_2F$: $HSbF_6$ catalyst caused vigorous gas evolution at room
          temperature. The starting ether was completely consumed in a short time. The
          gas evolved is presumably CH_2F_2, but this was not confirmed.
30

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f) $C_4F_9OC_3H_7$: With SbF_5 there is initial reaction to give the corresponding acid fluoride but reaction rapidly ceases due to catalyst deactivation. As with the $C_4F_9OC_2H_5$ above, the fluoropropane formed in the dealkylation may react with the catalyst to deactivate it at room temperature, although the detailed

5   mechanism of deactivation is not clear.

g) $C_6F_{13}OCF_2H$: With SbF_5 there is very rapid reaction to give $C_5F_{11}COF$ and CF_3H. The presence of the CF_3H was confirmed by gas cell infrared spectroscopy of the effluent gases.

10

h) $C_4F_9O(C_2F_4O)_2CF_2H$: As in (g) above there is very rapid reaction with SbF_5 to give $C_4F_9OC_2F_4OCF_2COF$ and CF_3H as the sole products.

i) $C_8F_{17}OCH_2CF_3$: With SbF_5 there is a very short initial reaction but the catalytic

15   activity is quickly lost and the material is not visibly consumed. There is no $C_7F_{15}COF$ detected by GLC of the methanol washed product (to form the methanol ester). Again, a lower temperature alkylation may still be successful.

j) $C_4F_9OCH_2Cl$: With SbF_5 there was an initial rapid reaction to produce the

20   C_3F_7COF but again the catalytic activity was quickly lost. With $HSbF_6$ there was initial vigorous evolution of gas but the catalyst quickly was deactivated and formed a red-brown solid of unknown composition.

k) $C_4F_9OCHCl_2$: With $HSbF_6$ there was essentially an identical reaction to that

25   observed in (j), rapid but short reaction with conversion of the catalyst to a red-brown solid.

Example 8: HSbF$_6$ acid catalyzed reaction of perfluoroethylisopropyl ketone with
methyl fluoride to produce 3-methoxy-perfluoro-2-methylpentane:
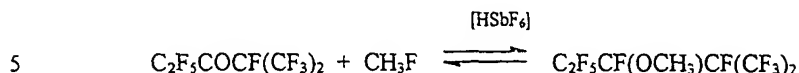
$$C_2F_5COCF(CF_3)_2 + CH_3F \xrightarrow{[HSbF_6]} C_2F_5CF(OCH_3)CF(CF_3)_2$$

5

A 600 mL Parr Bench Top Mini Reactor equipped with a mechanical stirrer,
thermocouple probe, dip tube, and pressure gauge was dried in an oven at 125 °C
for two hours. The ambient temperature reactor was reassembled after the addition

10   of 91 g of C$_2$F$_5$COCF(CF$_3$)$_2$ (Purity 99.6 %) and evacuated to 2 Torr at -78 °C.
The reactor was charged with 10 grams of HSbF$_6$ from a 150 mL monel cylinder.
While maintaining dry ice cooling on the reactor 48 g CH$_3$F (purity = 98⁺ %, PCR)
was charged to the reactor. Once all the reagents were charged, the reactor was
cooled with a dry ice bath overnight. A leak in the Teflon head seal developed

15   overnight, which was repaired and the reactor repressurized with helium. Gas
chromatographic analysis of a reaction aliquot sampled at -55 °C and quenched in
methanol as described in Example 1 indicated that 25 % of the starting material was
converted to product. The reaction was held over the weekend with a dry ice bath
and was at -6 °C when sampled as Aliquot 2. The reaction was cooled to -50 °C

20   and Aliquot 3 was taken. Another leak developed and the run was stopped. The
procedure employed to collect, quench, work up and analyze each reaction aliquot
was similar to that described in Example 1. The results of this study, including the
composition of the isolated fluorochemical phase and the calculated percent
conversion at each temperature are summarized in Table 6 below:

25

Table 6

Overall Reaction Time (min)	Reaction Temp. (°C)	Aliquot #	Fluorochemical Composition (by GC Area %)	Percent Conversion [ether]/([ether]+[ketone]) x 100
1020	-55	1	74.6% $C_2F_5COCF(CF_3)_2$ 25.0% $C_2F_5CF(OCH_3)CF(CF_3)_2$	Overall = 25.1%
2400	-6	2	96.6% $C_2F_5COCF(CF_3)_2$ 2.6% $C_2F_5CF(OCH_3)CF(CF_3)_2$	Overall = 2.7%
2505	-50	3	58.4% $C_2F_5COCF(CF_3)_2$ 41.5% $C_2F_5CF(OCH_3)CF(CF_3)_2$	Overall = 41.5%

This reaction shows that a substantial amount of perfluorinated ketone is
converted to ether product even under non-ideal conditions, *i.e.* low levels of CH_3F
5 due to gas leak. Aliquot 1 was analyzed by GC-MS to confirm product
identification.

Example 9: $HSbF_6$ catalyzed reaction of perfluoropropionyl fluoride with ethyl
fluoride to produce 1-ethoxy-perfluoropropane.
10
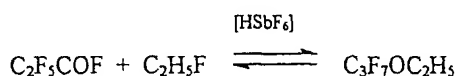
$$C_2F_5COF + C_2H_5F \overset{[HSbF_6]}{\rightleftharpoons} C_3F_7OC_2H_5$$

A 600 mL Parr Bench Top Mini Reactor equipped with a mechanical stirrer,
15 thermocouple probe, dip tube, and pressure gauge was cleaned with acetone and
evacuated to 1 Torr to remove residual acetone. The evacuated reactor was
charged with 101.5 g of liquefied C_2F_5COF (Purity 97 %; Major impurities include
1.5 % $CF_3CF_2OCF_3$ and 0.5 % *cyclo*-$CF_2CF_2CF_2O$) while maintaining dry ice
cooling. The reactor was then charged with 10 g $HSbF_6$ catalyst (Aldrich) per
20 Example 8 and cooled to -50 °C. While maintaining dry ice cooling, the reactor was
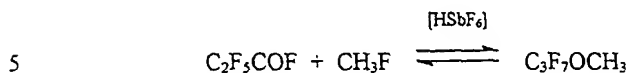charged with

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48 g of gaseous C_2H_5F (Purity = 97 % min, PCR) through the head space of the

reactor. Samples were taken at various temperatures per the procedure outlined in

Example 1, but using ethanol instead of methanol as the quenching agent. The

product distribution and percent conversion determined by GC analysis of the

5 fluorochemical phase isolated after water addition to the alcohol quench solution

are summarized in Table 7.

Table 7

Overall Reaction Time (min)	Reaction Temp. (°C)	Aliquot #	Fluorochemical Composition (by GC Area %)	Percent Conversion [ether]/([ether]+[ester]) X 100
15	-50	1	70.8 % $C_2F_5CO_2C_2H_5$ 18.3 % $C_3F_7OC_2H_5$ 10.5 % C_2H_5F 0.4 % Polyethylene oligomers	Overall = 20.5%
120	-64	2	63.3 % $C_2F_5CO_2C_2H_5$ 21.2 % $C_3F_7OC_2H_5$ 9.7 % C_2H_5F 0.4 % Polyethylene oligomers	Overall = 25.1%
1140	-37	3	54.0 % $C_2F_5CO_2C_2H_5$ 32.5 % $C_3F_7OC_2H_5$ 6.7 % C_2H_5F 6.8 % Polyethylene oligomers	Overall = 37.6%
1200	-37	4	54.3 % $C_2F_5CO_2C_2H_5$ 31.6 % $C_3F_7OC_2H_5$ 7.0 % C_2H_5F 7.1 % Polyethylene oligomers	Overall = 36.7%
1270	-42	5	61.7 % $C_2F_5CO_2C_2H_5$ 27.7 % $C_3F_7OC_2H_5$ 3.4 % C_2H_5F 7.2 % Polyethylene oligomers	Overall = 31.0%
1410	-58	6	49.8 % $C_2F_5CO_2C_2H_5$ 32.9 % $C_3F_7OC_2H_5$ 8.5 % C_2H_5F 8.8 % Polyethylene oligomers	Overall = 39.8%
1560	-55	7	51.8 % $C_2F_5CO_2C_2H_5$ 33.2 % $C_3F_7OC_2H_5$ 6.7 % C_2H_5F 8.3 % Polyethylene oligomers	Overall = 39.0%

This reaction shows that fluoroethane can be used as an effective alkylating agent in

10 this reaction although competing formation of polyethylene oligomers is observed

under the reaction conditions.

Example 10: HSbF$_6$ acid catalyzed reaction of perfluoropropionyl fluoride with
methyl fluoride to produce 1-methoxy-perfluoropropane:

$$C_2F_5COF + CH_3F \xrightleftharpoons{\text{[HSbF$_6$]}} C_3F_7OCH_3$$

5

A 600 mL Parr Bench Top Mini Reactor equipped with a mechanical stirrer,
thermocouple probe, dip tube, and pressure gauge was cleaned with acetone and
evacuated to 1 Torr to remove residual acetone. The reactor was charged with

10   11.3 g HSbF$_6$ catalyst (Aldrich) per Example 8 and cooled with dry ice. The
evacuated reactor was charged with 105.5 g of liquefied, sulfuric acid treated,
C$_2$F$_5$COF (Purity
97 %; Major impurities include 1.5 % CF$_3$CF$_2$OCF$_3$ and 0.5 % cyclo-CF$_2$CF$_2$CF$_2$O)
while maintaining dry ice cooling. [The sulfuric acid treatment of C$_2$F$_5$COF consists

15   of washing it with a 10 % weight charge of concentrated sulfuric acid in a clean dry
Parr reactor at ambient conditions for one hour. The C$_2$F$_5$COF is then transferred
to a clean dry stainless steel cylinder by one plate distillation from the reactor into
the dry ice cooled cylinder. The Parr reactor is heated to 30 °C to complete the one
plate distillation of the C$_2$F$_5$COF to the cylinder.] Following the addition of sulfuric

20   acid purified C$_2$F$_5$COF to the Parr reactor the reactor is charged with 43.5 g of
gaseous CH$_3$F (Purity = 98*% PCR) through the head space of the reactor while
maintaining dry ice cooling. Samples were taken at various temperatures per
Example 9. The overall GC results from this study are summarized in Table 8.

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Table 8

Overall Reaction Time (min)	Reaction Temp. (°C)	Aliquot #	Fluorochemical Composition (by GC Area %)	Percent Conversion [ether]/([ether]+[ester]) x 100
15	-50	1	48.2 % $C_2F_5CO_2C_2H_5$ 51.2 % $C_3F_7OCH_3$	Overall = 51.5%
1125	-47	2	20.8 % $C_2F_5CO_2C_2H_5$ 79.0 % $C_3F_7O\,CH_3$	Overall = 79.1%
1245	-64	3	38.1 % $C_2F_5CO_2C_2H_5$ 61.7 % $C_3F_7OCH_3$	Overall = 61.8%
1350	-46	4	13.7 % $C_2F_5CO_2C_2H_5$ 86.3 % $C_3F_7OCH_3$	Overall = 86.3%
1385	-30	5	11.5 % $C_2F_5CO_2C_2H_5$ 88.3 % $C_3F_7OCH_3$	Overall = 88.5%
1465	-37	6	6.4 % $C_2F_5CO_2C_2H_5$ 93.6 % $C_3F_7OCH_3$	Overall = 93.6%
2445	-19	7	40.0 % $C_2F_5CO_2C_2H_5$ 59.9 % $C_3F_7OCH_3$	Overall = 60.0%
2555	-41	8	6.1 % $C_2F_5CO_2C_2H_5$ 92.4 % $C_3F_7OCH_3$	Overall = 93.8%

This reaction provides high conversions to the desired ether products, and the catalyst lifetime is extremely long.

5

Example 11: SbF₅ catalyzed transalkylation reaction of pentafluoropropionyl fluoride with 2-H-octafluoroisobutylmethyl ether to produce heptafluoropropylmethyl ether.

10

$$C_2F_5COF + (CF_3)_2CHCF_2OCH_3 \overset{[SbF_5]}{\rightleftharpoons} n\text{-}C_3F_7OCH_3 + (CF_3)_2CHCOF$$
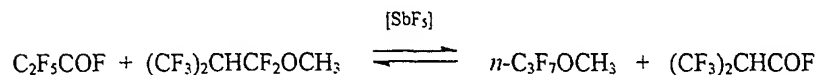
In a tubular, stainless steel pressure reactor pentafluoropropionyl fluoride (3.39 g, purity

15   97 %, 23 mmol), 2-H octafluoroisobutylmethyl ether (6.17 g, purity 98 %, 26 mmol) and antimony pentafluoride (Aldrich, 0.62 g, 3 mmol) were heated at 50-52 °C for 24 hours. A pressure of 9300 torr at 50 °C was achieved in 10 min after the reaction was begun and did not change upon further heating. The mixture was held overnight at -78 °C and then warmed to -10 to -15 °C for 5 hours. Methanol (3.1 g) was added at -78 °C, the

20   reactor was closed again, shaken and allowed to warm to room temperature for 30 min.

After dismantling the reactor, 13.0 g of slightly colored liquid was recovered. The crude product was washed twice with water and dried over $MgSO_4$ to obtain 9.92 g of a mixture comprising 27 % heptafluoro-n-propylmethyl ether (n-$C_3F_7OCH_3$); 1.3 % 2-H-octafluoroisobutylmethyl ether; 4.1 % methylpentafluoropropionate ($C_2F_5COOCH_3$) and

5   65% methyl-2H-hexafluoroisobutyrate $(CF_3)_2CHCOOCH_3$, by GC. The mixture was distilled to give 4.1 g n-$C_3F_7OCH_3$ (b.p. 34 – 52 °C; purity (GC) = 75 %) and 5.0 g $(CF_3)_2CHCOOCH_3$ (b.p. 76 – 90 °C; purity (GC) = 93.5 %; Product yields were calculated based upon the weight of starting materials charged and the weight of respective liquid product fractions isolated after correcting for purity as determined by

10   GC. The yield of $C_3F_7OCH_3$ was 68 % based upon pentafluoropropionyl fluoride and the yield of $(CF_3)_2CHCOOCH_3$ was 96 % based on 2-H-octafluoroisobutylmethyl ether. The structure of all compounds was confirmed by ^{19}F and ^{1}H NMR.
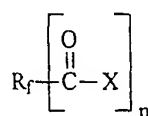

15

CLAIMS

1.   A process for the preparation of hydrofluoroether compounds, said process comprising:

5   (1) reacting in the presence of at least one Lewis acid catalyst or a mixture comprising Lewis acid and Brønsted acid catalysts:

        a) a fluorinated ketene or a fluorinated carbonyl-containing compound of the formula:

$$R_f \left[\begin{matrix} O \\ \| \\ C-X \end{matrix} \right]_n$$

10

wherein n is an integer equal to 1, 2 or 3; and

            when n is 1, R_f is a fluorine atom or is a fluorinated alkyl group having from
                1 to about 15 carbon atoms that may be substituted or unsubstituted,
                saturated or unsaturated, cyclic or acyclic, linear or branched and may
15   optionally contain one or more catenary heteroatoms;

            when n is 2, R_f is a fluorinated alkylene group having from 1 to about 15
                carbon atoms that may be substituted or unsubstituted, saturated or
                unsaturated, cyclic or acyclic, linear or branched and may optionally
                contain one or more catenary heteroatoms;

20   when n is 3, R_f is a fluorinated alkylidene group having from 1 to about 15
                carbon atoms that may be substituted or unsubstituted, saturated or
                unsaturated, cyclic or acyclic, linear or branched and may optionally
                contain one or more catenary heteroatoms; and

            wherein each non-fluorine substituent on the above R_f group may optionally
25   include -Cl, -H, -Br, -SO$_2$X, -SO$_2$R', -COX, -CO$_2$R', or -OR' where R' is
                a fluorinated or non-fluorinated alkyl group; and

            each X is independently a hydrogen or a halogen atom or is of the formula
                R'$_f$ or OR'$_f$ where R'$_f$ is a partially or fully fluorinated or non-fluorinated
                alkyl group having from 1 to about 10 carbon atoms that may be

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substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic,

linear or branched and may optionally contain one or more catenary

heteroatoms; where X is an R'_f group, that R'_f group may form a ring

with the R_f group previously defined; and

5

    b) an alkylating agent of the general formula:

R-F

wherein:

10   R is a substituted or unsubstituted, saturated or unsaturated, cyclic or

acyclic, linear or branched, non-halogenated or partially halogenated

alkyl group having from 1 to about 10 carbon atoms that can optionally

include one or more catenary heteroatoms, where if said R group is

substituted, the non-hydrogen substituents may optionally include -Cl, -

15   Br, -F, $-SO_2X$, $-SO_2R'$,

-COX', -COR', $-CO_2R'$, or -OR' where R' is a fluorinated or non-

fluorinated alkyl group and where X' is a halogen atom, and with the

proviso that when R is perfluorinated, the R-F compound has an

activated C-F bond; and

20

    (2) recovering hydrofluoroether from the resulting reaction mixture.
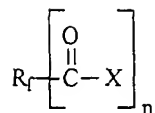

    2.   A process for the preparation of hydrofluoroether compounds, said process

comprising:

25   (1) reacting in the presence of at least one Lewis acid catalyst or a mixture

comprising Lewis acid and Brønsted acid catalysts:

    a) a fluorinated mono- or polyether compound with

    b) a fluorinated ketene or a fluorinated carbonyl-containing compound of

the formula:

30

$$R_f \left[\begin{matrix} O \\ \| \\ C-X \end{matrix} \right]_n$$

wherein n is an integer equal to 1, 2 or 3; and

when n is 1, R_f is a fluorine atom or is a fluorinated alkyl group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted,

5   saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally contain one or more catenary heteroatoms;

when n is 2, R_f is a fluorinated alkylene group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally

10   contain one or more catenary heteroatoms;

when n is 3, R_f is a fluorinated alkylidene group having from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally contain one or more catenary heteroatoms; and

15   wherein each non-fluorine substituent on the above R_f group may optionally include -Cl, -H, -Br, -SO$_2$X, -SO$_2$R', -COX, -CO$_2$R', or -OR' where R' is a fluorinated or non-fluorinated alkyl group; and

each X is independently a hydrogen or a halogen atom or is of the formula R'$_f$ or OR'$_f$ where R'$_f$ is a partially or fully fluorinated or non-fluorinated

20   alkyl group having from 1 to about 10 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally contain one or more catenary heteroatoms; where X is an R'$_f$ group, that R'$_f$ group may form a ring with the R_f group previously defined; and

25

(2) recovering hydrofluoroether from the resulting mixture.

3.   A process for the preparation of hydrofluoroether compounds, said process comprising:

(1) reacting in the presence of at least one Lewis acid catalyst or a mixture

comprising Lewis acid and Brønsted acid catalysts:

      a) a fluorinated mono- or polyether compound or a fluorinated

oxacycloalkane with

5   b) an alkylating agent of the general formula:
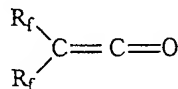

R-F

wherein:

      R is a substituted or unsubstituted, saturated or unsaturated, cyclic or

10   acyclic, linear or branched, non-halogenated or partially halogenated

      alkyl group having from 1 to about 10 carbon atoms that can optionally

      include one or more catenary heteroatoms such as oxygen, nitrogen or

      sulfur, where if said R group is substituted, the non-hydrogen

      substituents may optionally include -Cl, -Br, -F, $-SO_2X'$, $-SO_2R'$, -COX',

15   -COR', $-CO_2R'$, or -OR' (where R' is as defined above and where X' is a

      halogen atom) and with the proviso that when R is perfluorinated, the R-

      F compound has an activated C-F bond; and

      (2)   recovering hydrofluoroether from the resulting mixture.

20

4.   The process of claim 1 or 2 wherein said fluorinated carbonyl-containing

compound is a fluorinated acyl fluoride or a fluorinated ketone.

5.   The process of claim 1 or 2 wherein said fluorinated ketene is selected

25   according to the formula:

$$R_f \diagdown \atop R_f \diagup C = C = O$$

      where each R_f is selected, independently from one another, as a fluorine

30   atom or as a fluorinated, preferably perfluorinated, alkyl group having

from 1 to about 15 carbon atoms that may be substituted or unsubstituted, saturated or unsaturated, cyclic or acyclic, linear or branched and may optionally contain one or more catenary heteroatoms such as nitrogen, sulfur, or oxygen.

6. The process of claim 2 or 3 wherein said fluorinated mono- or polyether compound is of the formula:

$$R^1O(R^2O)_yR^3$$
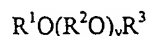
wherein y is 0 or is an integer greater than or equal to 1 and R^1, R^2, and R^3 each is independently selected as a non-fluorinated or a partially or fully fluorinated, substituted or unsubstituted, linear or branched, cyclic or acyclic, saturated or unsaturated alkyl group having from 1 to about 10 carbon atoms with the proviso that at least one of said R^1, R^2, or R^3 groups is fluorinated.

7. The process of claim 1 or 3 wherein said alkylating agent is CH_3F, C_2H_5F or CH_2F_2.

8. The process of any of the preceding claims wherein said catalyst is selected from the group of compounds consisting of: SbF_5, $HSbF_6$, TiF_4, $AlCl_xF_{(3-x)}$ ($x=0-3$), $SbCl_xF_{(5-x)}$ ($x=0-3$), $HF-BF_3$, TaF_5, NbF_5, AsF_5, BiF_5, ZrF_4, FeF_3, $SbCl_5$, $SbCl_2F_3$, $HOSO_2F/SbF_5$, and mixtures and combinations thereof with each other or with HF or FSO_3H.

9. The process of any of the preceding claims wherein said catalyst is supported on an inert substrate.

10. A hydrofluoroether made according to any of the preceding claims.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C07C41/01   C07C43/12   C07C41/14

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document. with indication, where appropriate. of the relevant passages	Relevant to claim No.
X	DE 12 94 949 B (FARBWERKE HOECHST) 14 May 1969 cited in the application see the whole document	10
A		1-9
X	FR 2 287 432 A (SOCIETE NATIONALE DES POUDRES ET EXPLOSIFS) 7 May 1976 cited in the application see claims	10
A		1-9
X	WO 96 36689 A (MINNESOTA MINING AND MANUFACTURING) 21 November 1996 cited in the application see page 4, line 28 - page 5, line 30	10
A		1-9

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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 October 1998	04/11/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Wright, M

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INTERNATIONAL SEARCH REPORT

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document. with indication.where appropriate. of the relevant passages	Relevant to claim No.
X	US 4 357 282 A (D. G. ANDERSON) 2 November 1982 cited in the application see examples	10
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/15886

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